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## Diffusion Time-Scale Invariance, Markovization Processes and Memory Effects in Lennard-Jones Liquids

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We report the results of calculation of diffusion coefficients for Lennard-Jones liquids, based on the idea of time-scale invariance of relaxation processes in liquids. The results were compared with the molecular dynamics data for Lennard-Jones system and a good agreement of our theory with these data over a wide range of densities and temperatures was obtained. By calculations of the non-Markovity parameter we have estimated numerically statistical memory effects of diffusion in detail.

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The motion of atoms and molecules in liquids is a typical example of a many-body problem. It is well known, however, that in contrast to gases and solids the physical mechanisms of transport processes in liquid matter is no well established [1]. In particular, for diffusive systems the role of memory effects induced by the disorder of the background medium is not investigated enough [2, 3]. There are different theoretical approaches and approximations for calculating transport coefficients [1, 4], in some of them they resort to time correlation functions (see, for example, [1, 3, 4, 5, 6]). The general approach of time correlation functions leads to calculation of exact expressions of transport coefficients for hydrodynamic equations. The similar expressions are known as the Green-Kubo relations.

In the present work we suggest a new approach to calculating transport properties based on the realization of idea of time-scale invariance of relaxation processes in liquids [7] by well-known Zwanzig-Mori's memory function formalism [8, 9]. Recently this idea has made

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it possible to explain the experimental data on slow neutron scattering in liquid cesium and sodium [7]. Here we have tested this approach on Lennard-Jones (LJ) liquids. As known, among a large set of dense fluids these systems are one of the most popular (base) for different investigations. So, diffusion coefficients of LJ liquids were calculated for a wide range of densities and temperatures, and then quantitative analysis of the memory effects in diffusion phenomena has executed. The obtained results are compared with the predictions of other theories [6] and the molecular dynamics data [10].

As known, the diffusion coefficient can be expressed in terms of the velocity autocorrelation function (VACF)

$$a(t) = \frac{\langle v_\alpha(0)v_\alpha(t) \rangle}{\langle v_\alpha(0)^2 \rangle} \quad (1)$$

by the relation

$$D = \frac{k_B T}{m} \int_0^\infty a(t) dt. \quad (2)$$

The latter is one of the Green-Kubo equations, relating the integrals of the correlation function to the transport coefficients [1]. Here  $k_B$ ,  $T$  and  $m$  are the Boltzmann constant, temperature and atomic mass, respectively.

On the other side, the generalized Langevin equation (GLE) for VACF can be written in the following way:

$$\frac{da(t)}{dt} = -\omega^{(2)} \int_0^t M_1(\tau) a(t-\tau) d\tau, \quad (3)$$

where  $M_1(t)$  is the first-order normalized memory function [ $M_1(t=0) = 1$ ] and  $\omega^{(2)}$  is the second frequency moment of VACF. This equation is obtained by the use of Zwanzig-Mori's projection operators formalism [8]. However, the projection operators technique allows to derive the whole chain of interconnected equations similar to the above mentioned equation. These equations contain the memory functions  $M_i(t)$  and the even frequency moments  $\omega^{(2i)}$  of higher orders, i.e.  $i = 1, 2, 3, \dots$ . This chain can be represented in terms of Laplace transforms as a continued fraction:

$$\begin{aligned} \tilde{a}(s) &= \int_0^\infty dt e^{-st} a(t) = [s + \omega^{(2)} \tilde{M}_1(s)]^{-1} = 1 / \left\{ s + \omega^{(2)} / \left[ s + (\omega^{(4)} / \omega^{(2)} - \omega^{(2)}) \tilde{M}_2(s) \right] \right\} \\ &= 1 / \left\{ s + \omega^{(2)} / \left[ s + (\omega^{(4)} / \omega^{(2)} - \omega^{(2)}) / (s + \dots) \right] \right\}, \end{aligned} \quad (4)$$

and Eq. (2) yields

$$D = \frac{k_B T}{m} \tilde{a}(s=0). \quad (5)$$

So, the problem of calculation of transport properties can be reduced to calculation of the certain memory functions  $M_i(t)$ . Although there are microscopic expressions and some formal prescriptions for memory functions calculations, it is prohibitively difficult for models like Lennard-Jones (LJ) liquid. A rich variety of model functions was proposed for this purpose, most of which have little physical justification. For example, hyperbolic secant memory was used to calculate velocity, transverse stress, energy current density correlation functions and the corresponding transport coefficients for LJ liquid [4]. The validity and justification of this approach was closely examined in work [11].

There is another more effective and powerful way to calculate transport coefficients of the diffusion constant type. This method was first suggested in work [12] to calculate self-diffusion in liquid argon, and used later in Ref. [13] to investigate viscosity effects in liquid argon. Here we use this approach to analyze diffusion time-scales and to calculate the diffusion coefficient in LJ liquid over a wide density and temperature ranges.

As known, the memory functions  $M_i(t)$  have characteristic time scales, which can generally be defined at fixed  $i$  by  $\tau_i = \tilde{M}_i(s=0) = \int_0^\infty dt M_i(t)$ , where  $\tau_i$  is the relaxation time of a certain correlation function  $M_i(t)$ . These time scales characterize the corresponding relaxation processes and can have different numerical values. Nonetheless, on a certain relaxation level, (for example, on the  $i$ th level) the scale invariance of the nearest interconnected relaxation processes can exist. We shall consider below the following approximation  $\tau_{i+1} = \tau_i$ . Physically it means the occurrence of time-scale invariance on the  $i$ th relaxation level.

In case of  $i = 0$  we have an approximate equality of VACF relaxation time  $\tau_0$  and the relaxation time of the first-order memory function  $\tau_1$ . Then, from Eq. (5) and the second equality of Eq. (4) at  $\tau_1 = \tau_0$  one can obtain

$$D = \frac{k_B T}{m} \left[ \frac{1}{\omega^{(2)}} \right]^{1/2}, \quad \omega^{(2)} = \frac{4\pi n}{3} \int_0^\infty dr g(r) r^2 \left[ \frac{3}{r} \frac{\partial U(r)}{\partial r} + r \frac{\partial}{\partial r} \left( \frac{\partial U(r)}{r \partial r} \right) \right], \quad (6)$$

where  $n$  is density,  $g(r)$  is radial distribution function and  $U(r)$  is interparticle potential.

At  $i = 1$  we obtain the equality of the relaxation times of first and second order memory functions [14]. In this case,  $\tau_2 = \tau_1$ , and from Eqs. (4) and (5) we have

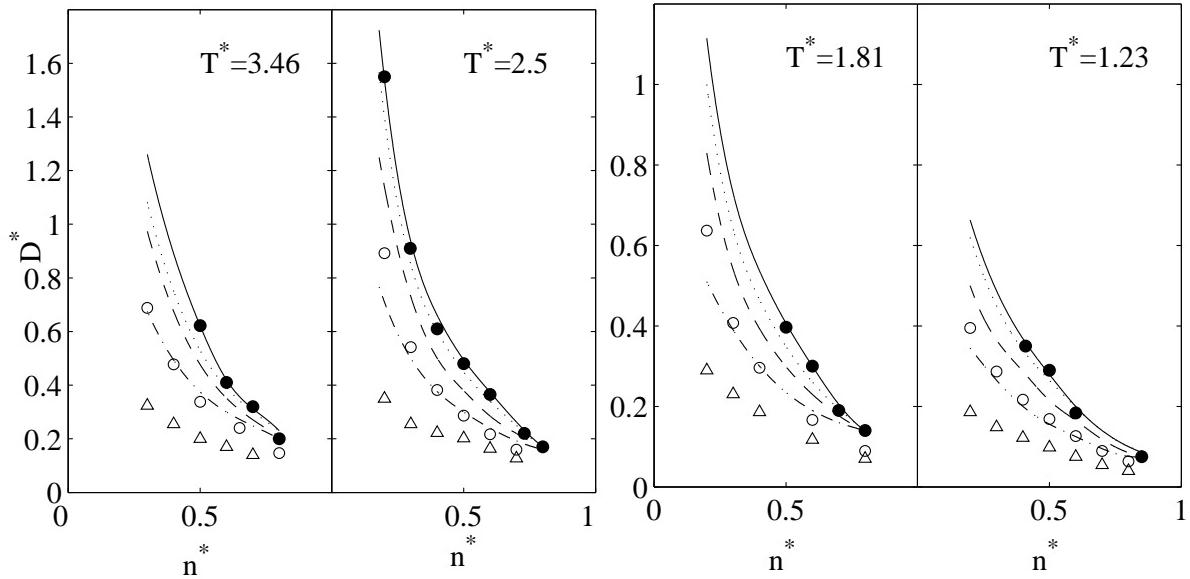


Figure 1: The reduced density  $n^* = n\sigma^3$  dependence of diffusion coefficient at the reduced temperature  $T^* = k_B T/\varepsilon = 3.46, 2.5, 1.81$  and  $1.23$ . The triangles ( $\triangle \triangle \triangle$ ) show results of Eq. (6), the solid line presents our results from Eq. (7), the circles ( $\circ \circ \circ$ ) show results of Eq. (8), the dotted line ( $\cdots$ ) presents the results of approximation with hyperbolic secant memory of Ref. [6], the broken ( $- - -$ ) and the chain line ( $- \cdot -$ ) correspond to results of two models for diffusion coefficient obtained on the basis of Joslin and Gray study in terms of the first two and three Mori's coefficients, correspondingly [6, 15]. The full circles ( $\bullet$ ) represent molecular dynamics data of Ref. [10] and correspond to diffusion values in points well within the fluid region of the LJ phase diagram [16]. Presented data bring out clearly that results of our theory are in excellent agreement with molecular dynamics data without any deviations.

$$\begin{aligned}
 D &= \frac{k_B T}{m} \frac{1}{\omega^{(2)}} \left[ \frac{\omega^{(4)}}{\omega^{(2)}} - \omega^{(2)} \right]^{1/2}, \\
 \omega^{(4)} &= \frac{8\pi n}{3m} \int_0^\infty dr g(r) \left[ 3 \left( \frac{dU(r)}{dr} \right)^2 + \left( r \frac{\partial}{\partial r} \left( \frac{\partial U(r)}{r \partial r} \right) \right)^2 + \frac{\partial U(r)}{\partial r} \cdot \frac{\partial}{\partial r} \left( \frac{\partial U(r)}{r \partial r} \right) \right] \\
 &\quad + \frac{8\pi^2 n^2}{3m} \int_0^\infty \int_0^\infty dr dr_1 r^2 r_1^2 \int_{-1}^1 d\beta g_3(\mathbf{r}, \mathbf{r}_1) \left[ \frac{3}{rr_1} \frac{\partial U(r)}{\partial r} \cdot \frac{\partial U(r_1)}{\partial r_1} \right. \\
 &\quad + \frac{r}{r_1} \frac{\partial U(r_1)}{\partial r_1} \cdot \frac{\partial}{\partial r} \left( \frac{\partial U(r)}{r \partial r} \right) + \frac{r_1}{r} \frac{\partial U(r)}{\partial r} \cdot \frac{\partial}{\partial r_1} \left( \frac{\partial U(r_1)}{r_1 \partial r_1} \right) \\
 &\quad \left. + rr_1 \frac{\partial}{\partial r_1} \left( \frac{\partial U(r_1)}{r_1 \partial r_1} \right) \cdot \frac{\partial}{\partial r} \left( \frac{\partial U(r)}{r \partial r} \right) \beta^2 \right], \tag{7}
 \end{aligned}$$

where  $g_3(\mathbf{r}, \mathbf{r}_1)$  is the triplet correlation function, and  $\beta$  is the cosine of the angle between  $r$  and  $r_1$ .

Following the same procedure for third and second order relaxation times,  $\tau_3 = \tau_2$  (and  $i = 2$ ), we come to the following expression:

$$D = \frac{k_B T}{m} \frac{[\omega^{(4)} - (\omega^{(2)})^2]^{3/2}}{[\omega^{(2)}]^{3/2} [\omega^{(6)} \omega^{(2)} - (\omega^{(4)})^2]^{1/2}}. \quad (8)$$

In a more general case with  $\tau_i = \tau_{i-1}$ ,  $i = 1, 2, \dots$  we can obtain the expression of diffusion coefficient by the first even frequency moments:  $\omega^{(2)}, \omega^{(4)}, \dots, \omega^{(2i)}$ . The second, the forth and the sixth frequency moments contained in Eqs. (6), (7) and (8) were approximately obtained for LJ liquid by authors [6]. Using these values, the diffusion coefficients were calculated with the help of Eqs. (6), (7) and (8). The comparison shows that the values of  $D$  obtained by Eq. (7) have the best agreement with the molecular dynamics data for the whole studied range of densities and temperatures. The results for  $D^* = D(m/\varepsilon\sigma^2)^{1/2}$  from Eq. (6) are presented in Fig. 1 as triangles, from Eq. (7) are shown as solid curves and from Eq. (8) are presented by circles. We also represented here the results of authors [6] for comparison with our ones. Namely, the diffusion coefficient obtained by Ref. [6] from the approximation of the second-order memory function by the hyperbolic secant are shown as dotted curves, whereas those obtained in Ref. [6] from the prescription of Joslin and Gray [15] are shown by broken and chain curves. From Fig. 1 one can easily see that the results of Eq. (7) have a better agreement with the molecular dynamics data [10, 16] presented by full circles in more cases than data found of others theories. This result is of great interest for the study of diffusion phenomena. It confirms the possibility of equality of relaxation times of first and second order memory functions, i. e.  $\tau_1$  and  $\tau_2$ . As can be seen from Fig. 1, the approximation with hyperbolic secant memory show a sufficiently satisfactory agreement for some cases. Joslin and Gray models yield an understated results in comparison with molecular dynamics data. The distinction between these theories and molecular dynamics data grows with decreasing of density. However, all examined models, including even Eqs. (6) and (8), begin to reproduce qualitatively molecular dynamics data as the triple point of LJ system with the reduced parameters  $n^* = 0.849$ ,  $T^* = 0.773$  is approached.

The next step of our study is estimation of statistical memory effects in diffusion processes of LJ liquid. It can be successfully done within the framework of memory function and *dimensionless* non-Markovity parameter [18] formalism. The last one is the ratio of

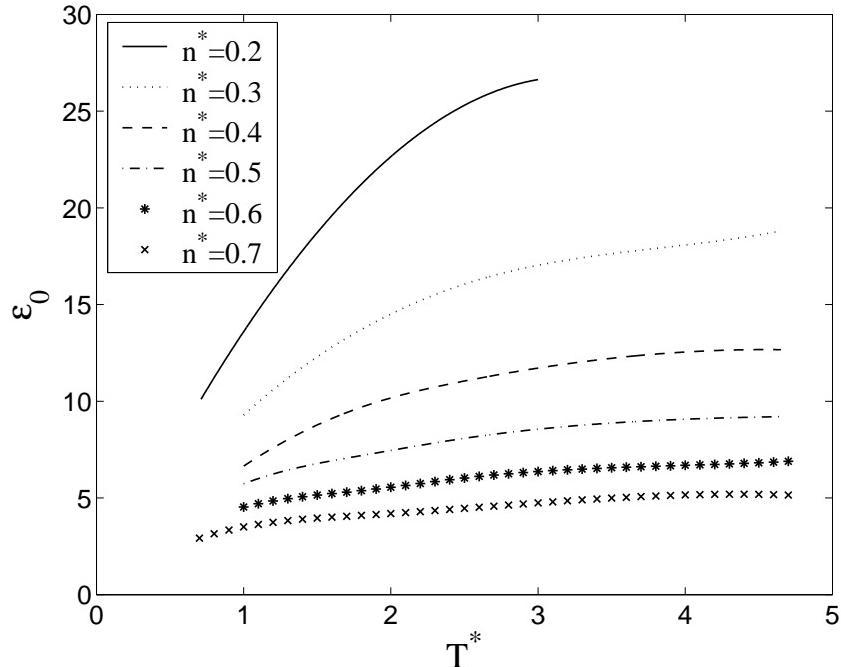


Figure 2: Variation of the non-Markovity parameter  $\varepsilon_0$  for VACF of LJ liquid with temperature at different densities. Correspondence between the curves and the densities is presented in the inset. The behavior of the parameter  $\varepsilon_0$  indicate a quantitative change of ratio between VACF time scale and memory relaxation time. The cross-over from Markovian ( $\varepsilon_0 \gg 1$ ) to a quasi-Markovian ( $\varepsilon_0 > 1$ ) character of the diffusion process at low temperature and high densities is noteworthy. Referring to the obtained data the diffusion process is in fact quasi-Markovian in a wide temperature region at high densities.

the relaxation time  $\tau_0$  of initial correlation function and the relaxation time  $\tau_1$  of memory function

$$\varepsilon_0 = \tau_0/\tau_1. \quad (9)$$

Using Eq. (5) for the relaxation time  $\tau_0 = \tilde{a}(s=0)$  we obtain

$$\tau_0 = \frac{mD}{k_B T}. \quad (10)$$

From the second equality in Eq. (4) at  $s = 0$  and Eqs. (9) and (10) we come to the final expression

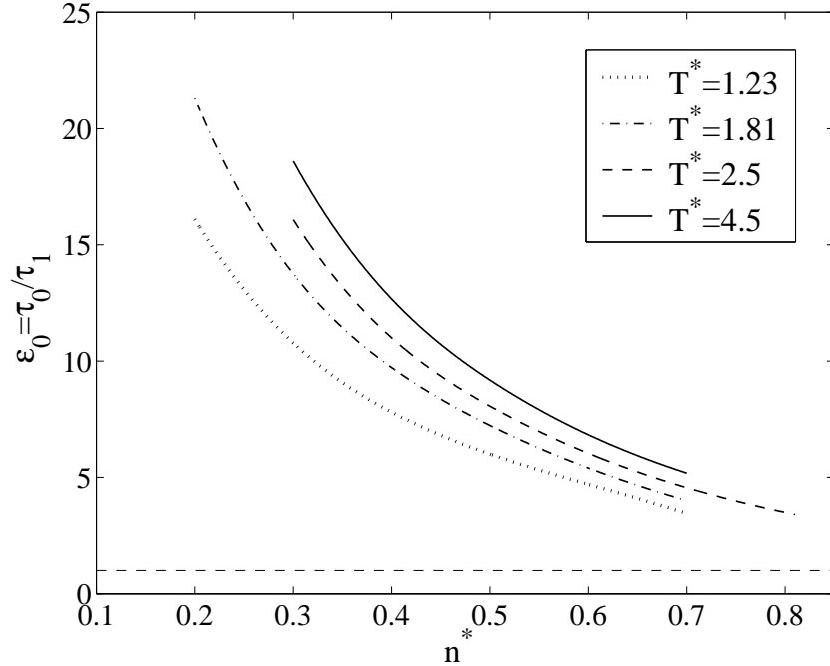


Figure 3: Variation of the non-Markovity parameter  $\varepsilon_0$  with the reduced density at four different temperatures  $T^* = 1.23, 1.81, 2.5$  and  $4.5$  reveal a nonlinear character of demarkovization at matter densifying. The horizontal dash line in the bottom of the figure corresponds to the quantitative value  $\varepsilon = 1$  (a full non-Markovian relaxation scenario). The markovization of the process occurs at decrease of density and increase of temperature; it is accompanied by increase of the parameter  $\varepsilon_0$  and partial disordering of LJ system. Increase of density results in ordering and demarkovization of diffusion process with sharp reduction of  $\varepsilon_0$  values.

$$\varepsilon_0 = \omega^{(2)} \left[ \frac{mD}{k_B T} \right]^2. \quad (11)$$

On the basis of the definition (9) it is possible to define the spectrum of non-Markovity parameter:  $\varepsilon_i = \tau_i/\tau_{i+1}$  (see Ref. [18] for a more detail). Then the general form of this parameter for  $i = 1, 2, 3, \dots$  can be expressed in terms of Mori's coefficients (static correlation functions) as

$$\varepsilon_i = \begin{cases} \frac{\Omega_2^4 \Omega_4^4 \dots \Omega_{i+1}^2 \tau_0^{-2}}{\Omega_1^4 \Omega_3^4 \dots \Omega_i^4}, & \text{if } i \text{ is odd,} \\ \frac{\Omega_1^4 \Omega_3^4 \dots \Omega_{i+1}^2 \tau_0^2}{\Omega_2^4 \Omega_4^4 \dots \Omega_i^4}, & \text{if } i \text{ is even.} \end{cases} \quad (12)$$

Obviously, the parameter  $\varepsilon_i$  obtained by Eq. (12) estimates the memory effects of the  $i$ th level relaxation process, which is described by the memory function  $M_i(t)$ .

To investigate the memory effects of VACF itself it is necessary to study the zero point in spectra of the non-Markovity parameter  $\varepsilon_0$  calculated by Eq. (11). Therefore, the parameter  $\varepsilon_0$  has been calculated for a wide range of densities and temperatures for LJ liquid. The results of our calculations are presented in Fig. 2. From this figure one can see that the non-Markovity parameter always satisfies condition  $\varepsilon_0 > 1$ . This is the evidence of weak statistical memory effects in diffusion processes, which is usually observed in Markovian and quasi-Markovian processes. In this case  $\tau_1$  is much smaller than the VACF relaxation time  $\tau_0$ . The received result helps to understand the reason of amazing efficiency of Markovian approximation in the analysis of diffusion in LJ liquids (see, for example, one of the recent investigations [19]). It also enables to estimate the source of unsatisfactory agreement of Eq. (6) with molecular dynamic data. The point is that Eq. (6) is based on the assumption of  $\tau_1 = \tau_0$  and/or  $\varepsilon_0 = 1$ , which is true for non-Markovian processes only, while Eqs. (7) and (8) are applied both to Markovian and non-Markovian phenomena. Furthermore, in Fig. 2 we can see, that the parameter  $\varepsilon_0$  smoothly increases with the increase of the reduced temperature  $T^* = k_B T / \varepsilon$ , at the same time it decreases with the increase of density. So, non-Markovian effects fall off (and/or Markovity is enhanced) when the temperature of the system increases while the value of the density  $n^* = n\sigma^3$  is fixed, i. e. markovization of processes is observed, and it reflects the amplification of randomness during diffusion. However, a "saturation" is attained at a certain value of temperature, and the values of the parameter  $\varepsilon_0$  almost cease to change in this case. As may be seen from Fig. 2, such "saturation" is observed at lower temperatures for a more dense medium. The density  $n^*$  dependence of the parameter  $\varepsilon_0$  is shown in Fig. 3 for the four isotherms. The behavior of these curves has a nonlinear character. In this figure we can observe demarkovization, that is, amplification of regularity and robustness in the system which appears with the increase of density. For example, for the isotherm  $T^* = 1.81$  the parameter  $\varepsilon_0$  decreases more than five times within density range  $0.2 \div 0.7$ . Non-Markovian effects are enhanced and begin to dominate in the vicinity of the triple point of LJ liquid, where a well-known negative correlation in the behavior of VACF is observed. The ratio between VACF time-scale and relaxation time of memory in this phase region is  $\sim 2.5 \div 5$ . This is a quantitative evidence of considerable memory effects incipient diffusion process of LJ system near the triple point, where the density variation is short ranged and of order of a couple of molecular diameters [20].

The results of this work can be summarized as follows. (i) We have presented a new approach in calculation of transport coefficients. The approach is based on the time-scale invariance idea, developed within framework of Zwanzig-Mori's formalism. Our theory allows to calculate transport properties in terms of frequency moments of corresponding correlation functions without any adjustable parameters. (ii) Three different expressions were obtained for the diffusion coefficient of LJ liquid and tested together with other theories and the molecular dynamics data over a wide range of densities and temperatures. The comparison showed that the equation obtained from the condition of approximate equality of relaxation times of the first- and second-order memory functions has the best agreement with the molecular dynamic data. This equation includes only the second and the fourth frequency parameters, which were calculated with a high degree of precision. (iii) The non-Markovity parameter calculated for the diffusion phenomena in LJ liquid reveals a Markovian character of thermal motions of particles. Finally, the values of this parameter demonstrate the cross-over from Markovian to quasi-Markovian relaxation scenario at low temperatures and high densities and allow to estimate quantitatively this cross-over.

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